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Redox Equilibria in the Cu^{2+}—Cu^{+}—Cu System in Water-Dimethylsulphoxide (*DMSO*) Mixtures

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The redox equilibria in the Cu^{2+}—Cu^{+}—Cu system have been studied in water-*DMSO* mixtures using the potentiometric and coulometric techniques. The formal potentials of the Cu^{2+}/Cu^{+}, Cu^{2+}/Cu and Cu^{+}/Cu couples as well as the equilibrium constants of the reproportionation reaction $Cu^{2+} + Cu = 2\,Cu^{+}$ were determined. Based on the potentials expressed in the ferrocene electrode scale, *Gibbs* free energies of transfer of Cu^{2+} and Cu^{+} from water to water-*DMSO* mixtures were calculated and discussed. A preferential solvation of Cu^{+} by *DMSO* was found.

(Keywords: Cuprous ion reproportionation; Ionic solvation; Mixed solvents; Redox equilibria; Transfer free energy)

Das Redox-Gleichgewicht am Cu^{2+}—Cu^{+}—Cu-*System in Wasser-Dimethylsulfoxid-Mischungen*

Das Redox-Gleichgewicht am Cu^{2+}—Cu^{+}—Cu-System wurde in Wasser-Dimethylsulfoxid-Mischungen mit Hilfe potentiometrischer und coulometrischer Methoden untersucht. Die Formal-Standardpotentiale der Cu^{2+}/Cu^{+}-, Cu^{2+}/Cu- und Cu^{+}/Cu-Redoxpaare sowie die Gleichgewichtskonstanten der Reaktion $Cu^{2+} + Cu = 2\,Cu^{+}$ wurden ermittelt. Auf Grund der auf die Ferrocen-Elektrode bezogenen Potentiale wurden die freien Überführungsenthalpien für Cu^{2+}- und Cu^{+}-Ionen vom Wasser zu Wasser-*DMSO*-Mischungen berechnet und diskutiert. Die Ergebnisse weisen auf eine bevorzugte Solvatation von Cu^{+}-Ionen mit *DMSO* hin.

Introduction

The equilibrium of the reproportionation reaction

$$Cu^{2+} + Cu \rightleftharpoons 2\,Cu^{+} \tag{1}$$

can be quantitatively described by a value of the constant

$$K = c^{2}_{Cu^{+}}/c_{Cu^{2+}} \tag{2}$$

The equilibrium of the overall reaction (1) incorporates equilibria of three redox couples: Cu^{2+}/Cu^{+}, Cu^{2+}/Cu, and Cu^{+}/Cu. The corresponding reversible potentials for the redox couples mentioned can be expressed by the *Nernst* equations in the following form:

$$E_{21} = E_{21}^{\circ\prime} + \frac{RT}{F} \ln (c_{Cu^{2+}}/c_{Cu^{+}}) \tag{3}$$

$$E_{20} = E_{20}^{\circ\prime} + \frac{RT}{2F} \ln c_{Cu^{2+}} \tag{4}$$

$$E_{10} = E_{10}^{\circ\prime} + + \frac{RT}{F} \ln c_{Cu^{+}} \tag{5}$$

where $E^{\circ\prime}$ denotes the formal potential of appropriate redox system. According to the *Luther* rule, the formal potentials considered are linked mutually with a dependence

$$2E_{20}^{\circ\prime} = E_{21}^{\circ\prime} + E_{10}^{\circ\prime} \tag{6}$$

When the reproportionation equilibrium is established, the potentials corresponding to individual redox couples are equalized, i.e. $E_{21} = E_{20} = E_{10} = E_{eq}$.

The equilibrium of the reaction (1) is strongly influenced by the medium, since ions participating in the process can be differently coordinated by solvent molecules or other ligands present in the solution. Most investigations dealt, however, with aqueous solutions containing non-complexing base electrolyte. As it is known from the literature [1, 2] that the value of the equilibrium constant K is very low in such media and equals about 10^{-6} mol dm^{-3}. In water this instability of Cu^{+} ions is due to their much weaker solvation relative to Cu^{2+}. More appreciable equilibrium shift to the right, i.e. in favour of Cu^{+} formation, could be achieved in the aqueous medium if Cu^{+} ions are transformed into stable complexes.

A significant enhancement of Cu^{+} stability has been observed in many non-aqueous solvents, and this phenomenon is usually attributed to the change in the nature of ion-solvent interactions. The equilibrium constant for the reaction (1) has been satisfactorily determined only in methanol [3, 4], acetic acid [5], acetonitrile (*AN*) [6–8], and *DMSO* [9–11]. Much less information has been published about the equilibrium considered in mixed solvents and only quantitative data on H_2O—CH_3OH [4] and H_2O—*AN* [7] systems are so far reported.

Recently, more attention has been paid to the electrode reactions of inorganic ions in non-aqueous and mixed solvents. It is known that dipolar aprotic solvents, like *DMSO*, are better solvating media for cations than water [7, 12–19]. This could reflect a change of redox properties of several systems, as the interaction of their components with a medium would be different in each case. It is worth to emphasize that Cu^+ ions should be fairly stable in *DMSO* because of the relatively high value of $K > 0.1\,\mathrm{mol\,dm^{-3}}$ for reaction (1) in this solvent.

The aim of this work has been to study the equilibrium of the reproportionation (1) in water-*DMSO* mixtures and to explain the changes observed by the solvation of cations participating in this reaction.

Experimental

DMSO (Merck) was stored over KOH for two days and then distilled under argon at reducted pressure to collect for the experiments about 50% of the distillate as the main fraction. Water was triply distilled. As a source of Cu^{2+} ions $Cu(ClO_4)_2 \cdot 6\,H_2O$ and $Cu(ClO_4)_2 \cdot 5$ *DMSO* were used. The hydrated salt was obtained from the corresponding basic carbonate (POCh, p.a.) by neutralizing with 60% $HClO_4$ (Merck, p.a.). The solid compound $Cu(ClO_4)_2 \cdot 5$ *DMSO* was prepared from copper(II) perchlorate hexahydrate and purified *DMSO* according to the method described by *Selbin* et al. [20], and then recrystallized from anhydrous acetone. Stock solutions of $Cu(ClO_4)_2$ were analyzed for copper by *EDTA* titration. Sodium perchlorate (Merck, p.a.) was dried at 140 °C for two days before use. Before experiments, solutions were de-aerated by passing pure argon presaturated with the solution investigated. During measurements, this gas was passed over the solution.

A home made platinum rotating disc electrode (RDE) with a geometric area of $0.785\,\mathrm{cm^2}$ was used as a generating electrode in coulometric experiments. The RDE was driven with a synchronous motor and the rotation frequency was controlled by means of a Zopan PFL-30 digital frequency meter. Platinum wire spirals served as indicator and counter electrodes. Potentials were measured vs. the aqueous saturated NaCl calomel electrode (SCE). It was connected to the electrolytic cell through an intermediate vessel filled with the studied solution. Experiments were performed in a three-compartment electrochemical cell. The main compartment held $20\,\mathrm{cm^3}$ solution. Sintered glass discs were used for separating the various compartments.

A Radelkis OH-404/A potentiostat-galvanostat with an OH-404/B integrator was used in the coulometric work. Potentials were measured using a Meratronik V-540 digital voltmeter.

All experiments were carried out at 25 ± 0.2 °C.

Results

Investigations were carried out by means of both the potentiometric and coulometric method. The solutions examined contained $5 \cdot 10^{-2}\,\mathrm{mol\,dm^{-3}}$ $Cu(ClO_4)_2$ and $1\,\mathrm{mol\,dm^{-3}}$ $NaClO_4$ used as a base electrolyte. Additionally, $10^{-2}\,\mathrm{mol\,dm^{-3}}$ $HClO_4$ was used in water-reach solutions (up to 4 mol% *DMSO*) to prevent Cu^+ hydrolysis. The composition of water-*DMSO* mixture was changed from pure water to pure *DMSO*.

Two kinds of experiments were performed. In the first one, a copper rod, freshly covered cathodically with Cu-layer, was immersed into the

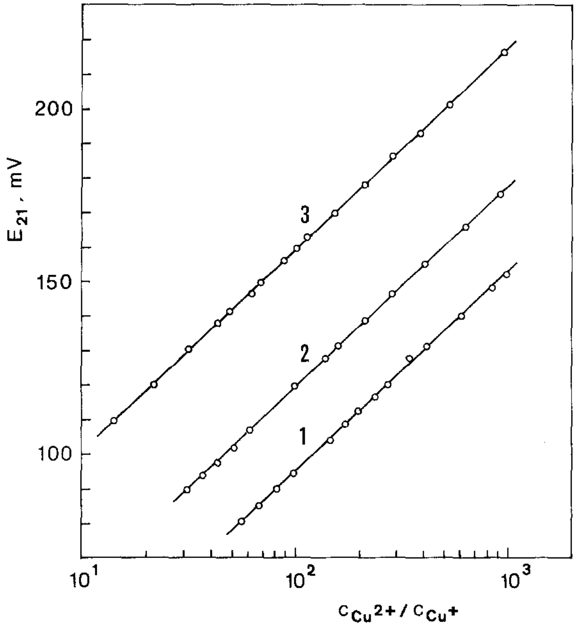

Fig. 1. The electrode potentials of the Cu^{2+}/Cu^+ couple, referred to the SCE(NaCl), as a function of the concentration ratio. Mole fraction of *DMSO* in water-*DMSO* mixtures: *1* 0.04; *2* 0.13; *3* 0.65

solution investigated. The reaction (1) was being conducted sufficiently long in order to establish an equilibrium in the Cu^{2+}—Cu^+—Cu system. The solution was stirred during the experiment. The reaction advancement was checked through measurement of the potential difference between the copper and platinum electrode, $\Delta E = E_{20} - E_{21}$. At equilibrium, i.e. when $\Delta E = 0$, the electrode potential, E_{eq}, was measured carefully vs. SCE.

In the other series of experiments, the formal potentials of the Cu^{2+}/Cu^+ couple were determined. For this purpose, electroreduction of Cu^{2+} was carried out under coulometric control at constant current using the platinum RDE. The generation was stopped at various time intervals, and the equilibrium potential of the Cu^{2+}/Cu^+ system, E_{21}, was measured.

Plots of E_{21} as a function of $\log(c_{Cu^{2+}}/c_{Cu^+})$ were linear with a slope of 59 ± 2 mV/decade which is in reasonable agreement with theoretical predictions for a reversible one-electron reaction. Some typical dependencies are shown in Fig. 1. The extrapolation of the plots to $c_{Cu^{2+}}/c_{Cu^+}$

Table 1. *The formal electrode potentials of the* Cu^{2+}/Cu^+, Cu^{2+}/Cu *and* Cu^+/Cu *couples, referred to aqueous SCE (*NaCl*), reproportionation constants, and Gibbs free energies of transfer for* Cu^{2+} *and* Cu^+ *ions*

x_{DMSO}	$E^{\circ\prime}_{21}$ mV	$E^{\circ\prime}_{20}$ mV	$E^{\circ\prime}_{10}$ mV	K $\mathrm{mol\,dm^{-3}}$	$-\Delta G^{\circ}_{tr}(Cu^{2+})$ $\mathrm{kJ\,mol^{-1}}$	$-\Delta G^{\circ}_{tr}(Cu^{+})$ $\mathrm{kJ\,mol^{-1}}$
0	−75	106	287	$7.7\cdot10^{-7}$		
0.02	−38	103	244	$1.7\cdot10^{-5}$	1	5
0.04	−20	101	222	$8.2\cdot10^{-5}$	3	8
0.13	3	98	193	$6.7\cdot10^{-4}$	10	14
0.22	12	89	166	$2.5\cdot10^{-3}$	18	20
0.34	23	83	143	$9.4\cdot10^{-3}$	27	26
0.43	34	81	128	$2.6\cdot10^{-2}$	31	29
0.54	39	74	109	$6.6\cdot10^{-2}$	38	34
0.65	43	67	92	$1.5\cdot10^{-1}$	42	37
1.00	51	67	83	$5.4\cdot10^{-1}$	49	41

= 1 allowed us to determine the formal potentials of the considered couple for different compositions of water-*DMSO* mixtures.

Additionally, the $c_{Cu^{2+}}/c_{Cu^+}$ values corresponding to the potentials E_{eq}, have been obtained from the discussed diagrams. Based on these values and taking into consideration the charge required for the conversion of the initial solution into the solution where $E_{21} = E_{eq}$, the corresponding concentrations of Cu^+ and Cu^{2+} were estimated and the formal potentials of the Cu^{2+}/Cu and Cu^+/Cu couples were calculated from eqn. (4) and (5), respectively.

The data obtained were employed to calculate the equilibrium constants K, either from eqn. (2) or from the following expression:

$$\ln K = \frac{2F}{RT}(E^{\circ\prime}_{21} - E^{\circ\prime}_{20}) = \frac{F}{RT}(E^{\circ\prime}_{21} - E^{\circ\prime}_{10}) \qquad (7)$$

The determined values of the formal potentials, expressed in respect to the aqueous SCE(NaCl), and K are listed in Table 1.

For pure *DMSO* solutions, values of K of the same order of magnitude were found by *Foll* et al. [9] in 0.1 *M* $LiClO_4$ (0.4) and could be also estimated from the potentiometric date given by *Ahrland* and *Persson* [11] in 0.1 and 1 *M* NH_4ClO_4 (0.68 and 0.15 respectively).

Discussion

The correlation between $\log K$ for the reaction (1) and the mole fraction of *DMSO*, x_{DMSO}, in water-*DMSO* mixtures is shown in Fig. 2. It results from this plot that K increases monotonically with the increase of

x_{DMSO} in whole composition range. It should be noted that K rises approximately 10^5 times within the $0 < x_{DMSO} < 0.5$ range, however a further enhancement of the *DMSO* content in solution does not cause so significant changes in K values. Such a dependence could be attributed to some preferencial solvation of Cu^+ ions and weaker solvation of Cu^{2+} by *DMSO* molecules in water-rich mixtures.

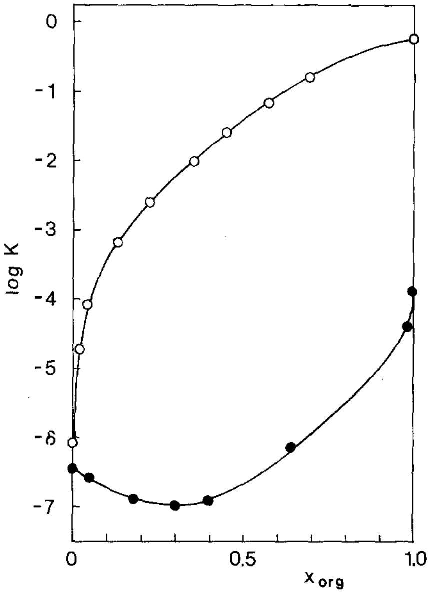

Fig. 2. The logarithm of the equilibrium constant for the reproportionation reaction (1) in mixtures of water with organic solvents: *DMSO* (open circles); methanol (black points). Data for water-methanol mixtures with 0.5 M H_2SO_4 as a background electrolyte taken from Ref. [4]

For comparison, Fig. 2 also contains the data of K obtained by *Yanov* and *Molodov* [4] for water-methanol mixtures. In this case, the value of K changes non-monotonically with a solvent composition and passes through a minimum at 30 mol% of CH_3OH. In the solutions of much higher CH_3OH content, more steep increase in the equilibrium constant, up to a value of $1.6 \cdot 10^{-4}$ mol dm^{-3} for pure methanol, is shown. Such a dependence of K on x_{CH_3OH} is likely due to the absence of specific interactions between Cu^+ ions and methanol molecules.

The discussed increase of the equilibrium constant can be elucidated if one takes into consideration the *Gibbs* free energy of transfer of Cu^{2+} and

Cu^+ ions from pure water to water-*DMSO* mixtures. This energy, $\Delta G^\circ_{tr}(Me^{n+})$, of a metal ion Me^{n+} can be calculated from the formal potential difference $\Delta E^{\circ\prime}$ of the Me^{n+}/Me electrode in both media, using the equation:

$$\Delta G^\circ_{tr}(Me^{n+}) = nF\Delta E^{\circ\prime} \tag{8}$$

It is important for the formal potentials considered, to be expressed versus such a reference electrode with potentials, which will not depend on the kind of solvent used. In such a way it is possible to eliminate the liquid junction potential between the aqueous calomel electrode and the solution investigated.

As a reference electrode which to some extent should fulfil this assumption, the Fic^+/Foc electrode [21] was chosen. The required potentials for the ferrocene electrode vs. SCE(NaCl) in water-*DMSO* mixtures have been interpolated from the data of *Galus* et al. [16, 22]. These data enabled us to recalculate estimated potentials for the Cu^{2+}/Cu and Cu^+/Cu systems into the ferrocene electrode scale, as well as to determine ΔG°_{tr} of Cu^{2+} and Cu^+ ions using equation (8). The values obtained in such a way have been presented in Fig. 3 and Fig. 4 as $E^{\circ\prime} = f(x_{DMSO})$ and $\Delta G^\circ_{tr}(Me^{n+})/n = f(x_{DMSO})$ dependencies. The values of ΔG°_{tr} for pure *DMSO* are in good agreement with the literature data [7, 11] which have been derived from the *TATB* extrathermodynamic assumption. It is obvious that the values of equilibrium constant K for the reaction (1) do not depend on any extrathermodynamic assumption.

The negative $\Delta G^\circ_{tr}(Me^{n+})$ values obtained indicate that *DMSO* acts as a stronger solvation agent than water on both the Cu^{2+} and Cu^+ ions. However, particular emphasis should be given to the fact that $\Delta G^\circ_{tr}(Cu^{2+})$ changes relative small if $x_{DMSO} < 0.15$ and becomes significant in the $0.2 < x_{DMSO} < 0.5$ range. This means that Cu^{2+} ions retain, at low *DMSO* concentrations, the solvation shell populated mainly by water molecules, which can be gradually replaced by *DMSO* molecules if the *DMSO* content is satisfactorily enhanced in the solvent mixture.

Contrary to that, a significant change in $\Delta G^\circ_{tr}(Cu^+)$ appears even at small *DMSO* concentrations in the mixture, $x_{DMSO} < 0.15$. This observation points to some preferential solvation of Cu^+ ions by *DMSO* molecules. On the other hand, it is known that these ions are rather poorly solvated in water [2].

These facts may be interpreted in terms of the *HSAB* concept [23]. According to this approach, the d^{10} Cu^+ ion should exhibit preferred interaction, as a soft acid, with the sulphur atom (soft base) of the *DMSO* molecule. It is very likely, that a tetrahedral structure of the *DMSO* molecule [24] will facilitate the formation of a $Cu^+ \cdots S$ bond.

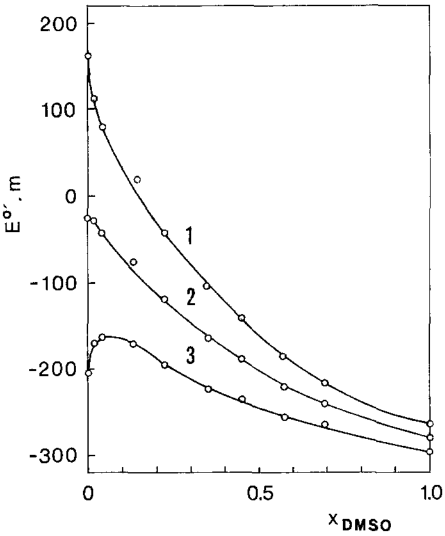

Fig. 3. The dependence of the formal potentials (expressed vs. the ferrocene electrode) for the Cu^+/Cu (*1*), Cu^{2+}/Cu (*2*) and Cu^{2+}/Cu^+ (*3*) couples on *DMSO* content in the mixed solvent

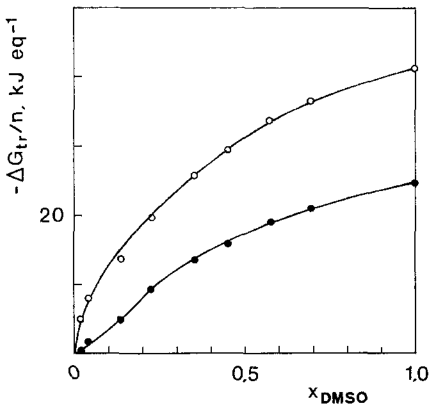

Fig. 4. The free energy of transfer per ionic charge of Cu^+ (open circles) and Cu^{2+} ions (black points) from water to water-*DMSO* mixtures, plotted against the mole fraction of *DMSO*

The changes in the free energy of transfer of both Cu^{2+} and Cu^{+} ions correspond to the redox equilibrium shift in the Cu^{2+}—Cu^{+}—Cu system. In the reproportionation reaction (1), the disappearing of one Cu^{2+} ion is accompanied by the formation of two Cu^{+} ions. Consequently, $RT\Delta \ln K = \Delta G^{\circ}_{\mathrm{tr}}(\mathrm{Cu}^{2+}) - 2\,\Delta G^{\circ}_{\mathrm{tr}}(\mathrm{Cu}^{+})$. It is remarkable that the absolute value of $\Delta G^{\circ}_{\mathrm{tr}}(Me^{n+})/n$ is much greater for Cu^{+} than that for Cu^{2+} in the whole *DMSO* concentration range. Thus, the transfer from water to water-*DMSO* mixtures is favourable to the stabilization of the monovalent state relative to the divalent one.

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